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ABSTRACT

The standard purification procedure for metallic halides does not include a pretreatment of the solid before melting. Such treatment is necessary in order to reduce the formation of corrosive hydrolysis products. It has been found that a dry LiCl-KCl eutectic mixture can be obtained by washing it repeatedly with liquid ammonia that has been treated with sodium metal.

INTRODUCTION

The standard preparation for a molten metallic halide usually involves the following procedure: the gradual heating of the salt at increasing temperatures in vacuum, the fusion of the salt and filtration through Pyrex glass wool, the washing of the melt with the appropriate hydrogen halide or halogen gas. These latter steps, i.e., filtration through glass wool and bubbling with hydrogen halide gases are carried out to eliminate the presence of oxides and hydroxides that form when the salt is heated in the presence of water. It is essential to remove these products since they account for the corrosive action of these melts on container materials.

One inherent difficulty in this procedure is the fact that there is essentially no treatment of the solid salt for the removal of water before

melting. It has been shown that, if a small percentage of hydrolysis products form upon melting, the washing with hydrogen halide gases cannot completely remove them.[1] The washing procedure is also hampered by some solubility of the hydrogen halide gas and its decomposition product, the halogen gas,[2] in the melt. Unless there is a period of prolonged evacuation and washing with an inert gas, such as dry nitrogen or argon, the presence of the residual soluble gas will be a complicating factor in the addition of metals to metallic halide melts treated in this manner.

In order, therefore, to reduce the possibility of hydrolysis as a result of heating the salt in the presence of water and in order to reduce the presence of hydrogen halide and halogen gases in the melt, a procedure has been devised that involves the treatment of the solid before melting. In this method, the salt is washed repeatedly in an evacuated system with liquid ammonia. The liquid ammonia is itself dried by treatment with alkali metals.

EXPERIMENTAL

Test for Presence of Water in Salt

A test for the presence of water vapor in a system is the visual observation of a gray film of potassium obtained by distilling the metal under vacuum ($<10^{-6}$ mm Hg). The occurrence of a blue film of potassium

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[1] H. Laitinen, W. Ferguson, and R. Osteryoung, J. Electrochem. Soc., 104, 516 (1957).

[2] B. R. Sundheim and J. Greenberg, J. Chem. Phys., 29, 1029 (1958).

under the same vacuum conditions indicates the absence of water vapor. The stability of the blue film indicates a highly inert system.[3]

Treatment of the Solid

The system shown in fig. 1 was placed on the vacuum line measuring a pressure less than 10^{-6} mm Hg and pumped on for 24 hours. Then liquid ammonia, which had been dried over sodium in a second ampule on the vacuum line, was distilled into the system containing the salt. A saturated solution was formed that was allowed to set for 24 hours at -78° C. Then the ammonia was redried by distilling it back into the second ampule containing sodium. The washed salt was then pumped on again to remove most of the residual ammonia. Any remaining ammonia was then condensed into a cold trap at liquid-nitrogen temperature and removed from the system. After the system was pumped overnight, the washing procedure was repeated two more times as described above. The third washing was done in the presence of a potassium film in region A (fig. 1).

Test for Inertness of Salt System

After the third washing, the potassium film was distilled along the surface of region B with a yellow flame (while pumping) to see whether a blue coloration could be obtained indicating the absence of water in the salt.

RESULTS

In the presence of the eutectic mixture LiCl-KCl, it was not possible to obtain a blue film by simply distilling the metal under vacuum.

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[3] J. F. Dewald and G. Lepoutre, J. Am. Chem. Soc., 76, 3369 (1954).

This was presumably due to water in the salt. Simply pumping on the salt and heating under vacuum conditions were not sufficient to completely remove the last traces of water, as indicated by the absence of a blue film upon distillation of the metal. This result is in agreement with the observations made by Burkhard and Corbett.[4]

When, after the third washing, the potassium film was distilled from region B with a yellow flame (while pumping), a stable blue film coating the surface of the salt was observed.

CONCLUSION

It is necessary that water be removed from the salt system before heating in order to reduce the formation of hydrolysis products. Repeated washings of the LiCl-KCl eutectic mixture with liquid ammonia produced a salt that, upom melting, did not adhere to the Pyrex container walls. As a sensitive test for the dryness of the salt, the solid mixture was exposed to heated potassium metal vapor. A stable blue film was observed on the surface of the solid salt mixture, indicating extreme dryness of the salt.

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[4] W. J. Burkhard and J. D. Corbett, United States Atomic Energy Commission ISC-929, Iowa State College, Ames Iowa, July 1957.

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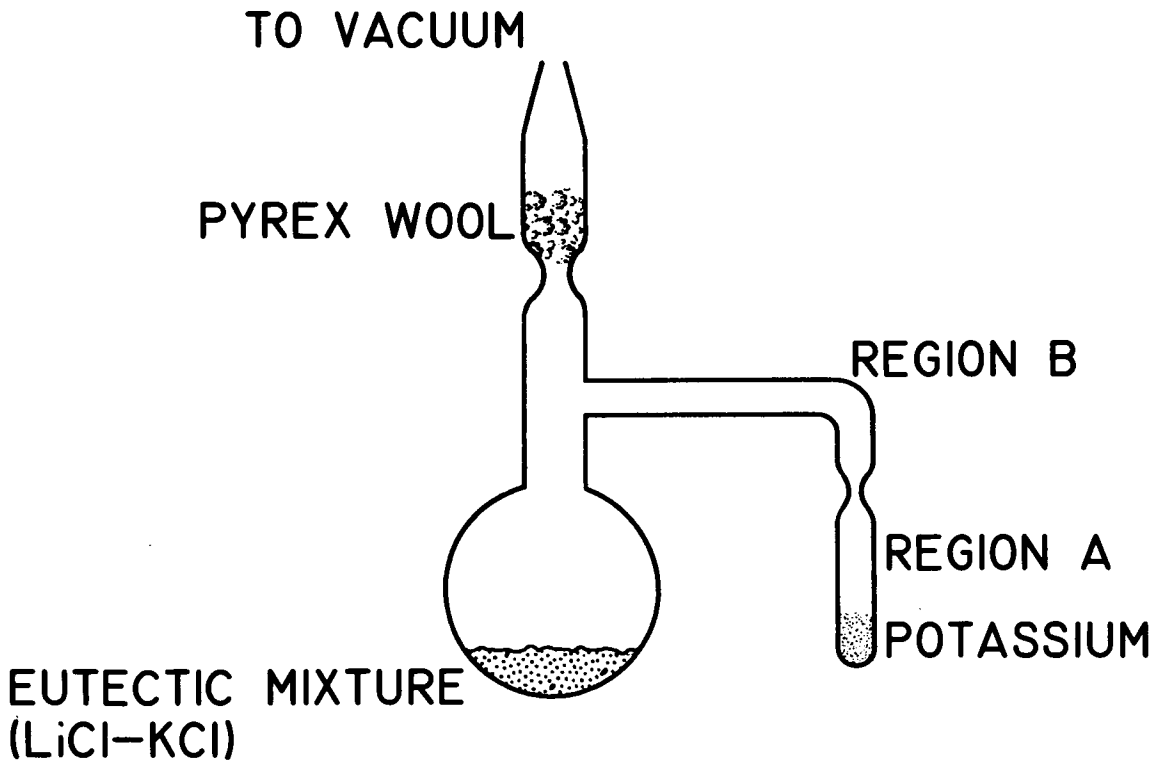

Fig. 1. - Typical system for preparation of dry salt mixture.